II. "On the successive Action of Sodium and Iodide of Ethyl upon Acetic Ether." By E. FRANKLAND, F.R.S., and B. F. DUPPA, Esq., F.R.S. Received January 13, 1870.

In a paper by Mr. J. Alfred Wanklyn, bearing the above title, and published in the Proceedings of the Royal Society, vol. xviii. p. 91, the author refers to our memoir on the same subject printed in the Philosophical Transactions for 1866, vol. clvi. p. 37, and expresses his opinion that our interpretation of the nature of the reaction must be erroneous because it involves the disengagement of hydrogen. This opinion is founded upon certain experiments which Mr. Wanklyn has himself made, and which are described in the number of Liebig's 'Annalen' for January 1869, and in the Chemical Society's Journal, vol. ii. p. 371.

In reference to this opinion we have to remark, first, that it is founded upon experiments which differ essentially from our own; and, second, that even the results obtained in those experiments by the author do not warrant the conclusion, at variance with ours, which he has drawn from them, viz. that the evolution of hydrogen in this reaction is inadmissible.

The reaction, the theoretical explanation of which Mr. Wanklyn seeks to controvert, is described in the Philosophical Transactions, vol. clvi. p. 38, as follows:—"When acetic ether is placed in contact with sodium it becomes hot, and a considerable quantity of gas is evolved, which, after being passed first through alcohol and then through water, burns with a non-luminous flame, and the products of combustion do not produce the slightest turbidity on agitation with baryta-water. In fact the gas is pure hydrogen. When the action is complete, the liquid solidifies on cooling to a mass resembling yellow beeswax. By putting the sodium into the acetic ether as just described, it is difficult to conduct the operation to completion, owing to the liquid gradually assuming such a thick and pasty condition as to prevent the further action of the sodium." Owing to the difficulty of carrying the reaction far enough in this way we frequently employed a modification of this process, which is minutely described in the same memoir. The modification consisted in placing the sodium in a separate vessel and causing the acetic ether to distil continuously over it; thus the portions of acetic ether still unacted upon were brought, again and again, into contact with the sodium, whilst the non-volatile product of the operation was retained in a lower vessel. As we acted upon several pounds of acetic ether at once, the operation frequently lasted several days, and *during the whole time torrents of hydrogen were evolved.* The temperature of the liquid in the distillation vessel was allowed to rise to 130° C., and the amount of sodium consumed was not much less than one atom for each molecule of acetic ether employed.

We have made several attempts to determine quantitatively the volume of hydrogen given off from a known weight of sodium, and also from a known weight of acetic ether, but in neither operation could we obtain a

trustworthy result. In the first case because the sodium, which fuses during the reaction, breaks up into a vast number of very minute globules, the final disappearance of which in the highly coloured and pasty product it is impossible to verify. In the second case because the thickening of the liquid prevents the reaction being pushed far enough to decompose the whole of the acetic ether employed. In a quantitative experiment, in which 4·857 grammes of acetic ether were acted upon by sodium in slight excess, 344·79 cub. centims. of hydrogen at 0° C. and 760 millims. pressure were obtained. If one molecule of acetic ether had lost one atom of hydrogen, 615·9 cub. centims. of gas ought to have been collected. It was evident, however, that a large proportion of acetic ether still remained unattacked at the close of the experiment.

Such, then, was our mode of operating; the hydrogen evolved was allowed freely to escape, the whole process was conducted at the ordinary atmospheric pressure, and the temperature varied from the boiling-point of acetic ether to 130° C. Moreover the acetic ether used was prepared with the greatest care so as to ensure the absence of alcohol and water. By our method of preparation, described in the memoir already cited, no traces of the former could be detected even in the crude ether; nevertheless it was first placed for several days over fragments of fused calcic chloride, which apparently remained perfectly dry and unaffected; it was then in some cases boiled for ten days or a fortnight upon many pounds of sodium-amalgam, which we find to be entirely without action upon pure acetic ether, whilst it rapidly attacks and removes alcohol, if the latter be added even in very small proportion to the acetic ether. When acetic ether, so treated and then distilled from the sodium-amalgam, was brought into contact with the sodium, an abundant evolution of hydrogen immediately commenced, and continued during the entire treatment, which, as already remarked, frequently lasted several days. The general impression, however, produced upon us by the whole of our operations was, that the evolution of hydrogen was not quite so great as that theoretically required by the reactions which we believe to take place; nevertheless it was obvious that no equations, from which free hydrogen was excluded, could possibly correctly express the chemical changes effected in this action. Certain experiments were undertaken to trace the missing hydrogen, but as they have not hitherto been completed we will not further allude to them here.

We now turn to Mr. Wanklyn's mode of experimenting. This is not stated in his communication to the Royal Society, but is given in the Journal of the Chemical Society, vol. xvii. p. 371, and in the Ann. Chem. u. Pharm. for January 1869, as follows:—

*Exp.* 1. "I sealed up a quantity of sodium with acetate of ethyl, *which had been very carefully deprived of alcohol and water*, and weighed the tube containing these materials. I then heated the tube to 130° C. for some time, until the contents had changed from liquid to solid. After opening the tube and allowing any gas that might have formed to escape, I weighed it again. *The loss amounted to* 0·5 *in* 100 *parts of acetic ether.*"

*Exp.* 2. "5 cub. centims. of good acetate of ethyl and 0·3 grm. of sodium were sealed up in a small glass tube and heated in a water-bath to 100° C. until all the sodium had disappeared. The tube was then opened under water; *the evolved gas measured* 25 cub. centims. at ordinary temperature, but at 0° C. and 760 millims. pressure and dry it measured 23 cub. centims. If the volume of hydrogen be calculated, which is equivalent to 0·3 grm. sodium, it will be found to be 140 cub. centims."

*Exp.* 3. "Another specimen of acetic ether, which was prepared with greater care, evolved no gas by the action of potassium or sodium."

It is thus evident that whilst we allowed all evolved gas freely to escape, Mr. Wanklyn operated in sealed tubes under great pressure,—an alteration in the conditions of the experiment which might well lead to a modification of the result. Mons. L. Cailletet has recently shown that the evolution of hydrogen from zinc and hydrochloric acid is gradually diminished and finally stopped under increasing pressure; and the same chemist also finds that the evolution of hydrogen from sodium-amalgam and water is diminished and finally stopped in a sealed tube. It follows from these experiments that pressure retards or even interrupts a reaction in which a permanent gas is evolved, whilst it is known to exercise little or no influence upon other chemical changes in which no evolution of gas takes place. This influence of pressure upon certain kinds of chemical action affords an explanation of the difference between the results of Mr. Wanklyn's experiments and our own, as regards the evolution of hydrogen during the action of sodium upon acetic ether. We can confirm his observation that sodium dissolves in valeric ether, under ordinary atmospheric pressure, without the evolution of any gas. A reaction, whatever its nature may be, which thus proceeds readily with ethylic valerate can scarcely be impossible with its homologue, acetic ether, and it is probable that this reaction goes on side by side with those which we have described in our memoir; but when the pressure is moderate those changes chiefly take place which involve the disengagement of hydrogen, whilst under the great pressure arising in sealed tubes these changes are more or less suppressed, and the reaction observed by Mr. Wanklyn comes into prominence.

Lastly, Mr. Wanklyn's own experiments scarcely justify his unqualified opinion that "equations which assume evolution of hydrogen in these reactions are inadmissible." In two out of three of his experiments, hydrogen in considerable quantity was evolved; and although in experiment No. 2, given above, he attributes the hydrogen to the presence of alcohol, yet in experiment No. 1 its origin cannot be so explained, as he states expressly that the acetic ether employed "had been very carefully deprived of alcohol and water;" yet the proportion of hydrogen evolved in this case was much larger than in experiment No. 2.

We reserve our observations upon Mr. Wanklyn's views regarding the changes which take place when sodium acts upon acetic, butyric, and valeric ethers, until the publication of the experimental data upon which those views are founded.